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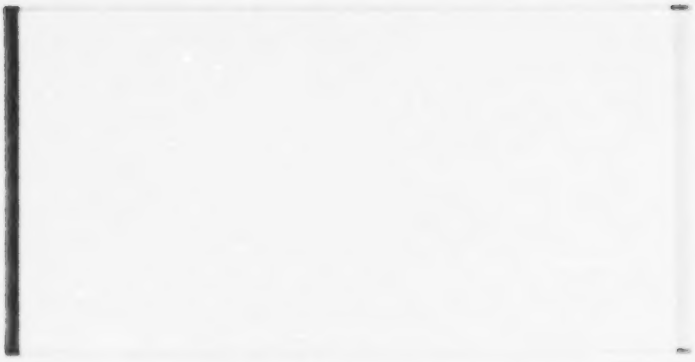

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FURNACE LIMESTONE INJECTION FOR SO_x CONTROL

Report No 85-108-K

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ABSTRACT

The results of a literature review of the dry limestone furnace injection process for reduction of SO_x emissions from coal-fired boilers are presented. The history of the process, sorbents used, chemistry, factors affecting the efficiency of SO_x removal and the handling and disposal of the waste materials are discussed.

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EXECUTIVE SUMMARY

FURNACE LIMESTONE INJECTION FOR SO_x CONTROL

A. Kalvins

A literature review of the dry limestone furnace injection process for reduction of SO_x emissions from coal-fired boilers is presented. The process involves injection of a calcium-based material, eg, limestone, directly into the coal-fired boiler. In the boiler the limestone is rapidly calcined to give CaO which reacts with SO_2 to form $CaSO_4$. The $CaSO_4$, along with any unreacted lime, is collected with the fly ash in a baghouse or electrostatic precipitator.

The efficiency of the process is generally low, approximately 50% SO_2 removal for stoichiometric ratios of sorbent:sulfur of <2. The efficiency is however critically affected by a number of factors. These factors include:

i) the composition of the coal,

ii) furnace temperature at the point of sorbent injection,

iii) retention or residence time of particles in the furnace,

iv) mass transfer between SO_2 in the flue gas and sorbent particle,

v) sorbent feed rate,

vi) sorbent: coal sulfur stoichiometry,

vii) sorbent particle size.

The extent to which each of these variables affects SO_2 removal is discussed in the report.

Despite the low efficiencies reported to date, the ease with which the technique can be applied to existing power plants and the relatively low cost of running the process (cf, wet flue gas desulfurization) have encouraged researchers to study ways of optimizing the technique.

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To Mr. F.J. Kee
Director of Research

FURNACE LIMESTONE INJECTION FOR SO_x CONTROL

1.0 INTRODUCTION

Injection of dry sorbent into the cavity of a coal-fired furnace is one of a number of options available for the reduction of SO_2 emissions. Other methods of control of SO_2 emissions from fossil fuel-fired power plants include:

- wet flue gas desulfurization (wet scrubbing)
- spray dryer flue gas desulfurization
- coal blending, and
- coal washing.

Wet scrubbing involves bringing an aqueous alkali slurry or solution, frequently lime or limestone, into direct contact with the flue gas. The alkali reacts with the SO_2 and a calcium sulfite sludge is formed. Wet flue gas desulfurization (FGD) systems have proved to be among the most costly and least reliable pieces of equipment in the utility industry. They suffer severe corrosion and plugging problems, and use a substantial percentage of the power generated by the plants they serve/1/.

In the spray dryer based FGD process, the hot flue gas leaving the boiler enters a spray dry chamber. Here the gas mixes with an atomized alkali slurry or solution. The hot gas evaporates the water in the slurry/solution and the SO_2 in the flue gas reacts with the alkali to give dry sulfite and sulfate particles. This method, like wet FGD, involves handling of a corrosive sorbent slurry/solution and requires purchase of specialized equipment. It may, however, be a lower capital cost alternative to wet scrubbing/2/.

In contrast to these two techniques, injection of dry sorbent into a boiler is a much simpler, albeit less effective method of SO_2 control. The process involves injection of a pulverized calcium-based material such as limestone ($CaCO_3$) or calcium hydroxide (hydrated lime, $Ca(OH)_2$) directly into the furnace cavity of a coal-fired boiler. The sorbent, once injected, rapidly decomposes to form a porous microstructure with a greater exposed surface area. The resulting lime particles are highly reactive and chemically combine with SO_2 to form solid $CaSO_4$. The $CaSO_4$ along with any unreacted lime is collected with the fly ash in a baghouse or electrostatic precipitator (ESP)/2/. The process is entirely dry and utilizes conventional equipment already present

85-108

at and familiar to power plant operators for the storage, handling and injection of the sorbent materials/2/. Sorbent costs and utilization efficiency have the greatest impact on the dry sorbent injection process, not system hardware as is the case with wet and spray dryer FGD methods. Limestone is the preferred sorbent from the standpoint of availability and cost. Recent laboratory studies and large-scale exploratory tests indicate the high potential of this process as a low-cost option for SO_2 control/2/.

This report presents the results of a literature review of the dry limestone furnace injection process. Topics discussed include the history of the process, sorbents used, the chemistry, factors affecting SO_2 removal efficiency and the handling and disposal of waste materials. Topics requiring further investigation are identified.

2.0 HISTORY

Dry sorbent injection into a coal-fired furnace was first reported in the 1950's/3/. Trial runs in laboratory furnaces and full-scale utility boilers in the United States, Europe and Japan during the 1960's, however, yielded only low levels (~20%) of SO_2 removal. These results were discouraging in view of the fact that SO_2 removal efficiencies of 90% had been hoped for. Removal efficiencies were, however, very dependent upon boiler design and operation, the type of sorbent and the injection system.

One cause of poor SO_2 removal was believed to be deadburning of sorbent (limestone) as a result of high boiler temperatures. This theory was supported by the observation that when limestone was injected into tangentially and arch-fired boilers, which have lower peak furnace temperatures than wall-fired boilers, sulfur removal by the sorbent improved. Sulfur capture levels of ~50% for stoichiometric ratios of sorbent:sulfur of <2 were recorded/4/. Nevertheless, the relatively low and variable SO_2 removal efficiencies combined with boiler operational concerns essentially discredited the sorbent injection method. In the early 1970's study of dry sorbent furnace injection was abandoned and the development of wet scrubber systems became the primary focus of SO_2 control efforts.

Nevertheless, interest in dry sorbent furnace injection was revived in the mid-1970's due in part to work carried out in Germany/3/. These studies involved injection of limestone into furnaces burning lignite and "brown" coal. SO_2 removal efficiencies of 75% were recorded at sorbent to sulfur ratios of 2:1 and no boiler slagging or fouling problems were observed. The dramatic improvement in SO_2 removal relative to previous studies was ascribed to the lower combustion temperatures and the larger volumes of brown coal burning furnaces. Brown coal has a high moisture content, thereby lowering furnace temperatures and the boilers are larger than average to accomplish the same heat transfer thereby increasing sorbent residence times in the furnace. These results suggested that by controlling combustion

conditions, ie, firing temperatures and sorbent-flue gas mixing, satisfactory SO_2 removal can be obtained with dry sorbent furnace injection at practical sorbent injection rates. The Europeans believed that dry calcium sorbent injection combined with coal cleaning or coal blending could provide a low cost method of SO_2 control.

The introduction of regulations limiting NO_x emissions and the growing incentive for low cost incremental SO_2 control applicable to existing power plants also helped to rekindle interest in dry sorbent furnace injection. The low NO_x requiring regulations resulted in the development of combustion techniques which lower peak flame temperatures in the boiler and improve control over mixing conditions. Many of the furnace conditions limiting NO_x formation are also necessary for efficient SO_2 removal via dry sorbent injection.

At present considerable research in the field of SO_2 control using dry sorbent furnace injection methods is in progress and a brief review of the results is presented in the following sections.

3.0 SORBENTS

The sorbent most often considered for the furnace injection process is limestone. Limestone is a general term embracing carbonate rocks or fossils. Limestone is composed primarily of calcium carbonate or combinations of calcium and magnesium carbonate with varying amounts of impurities. The most common impurities are silica and alumina. The two most fundamental types of limestone are high calcium and dolomitic. High quality high calcium limestone is 97-99% $CaCO_3$. Dolomitic limestone contains 40-43% $MgCO_3$, 49-54% $CaCO_3$ and 1-3% impurities. The term dolomite is generally loosely used and any carbonate rock containing $\geq 20\%$ $MgCO_3$ is often referred to as a dolomite.

The utility of limestone-based sorbents such as the hydrated species, high calcium hydrate (calcium hydroxide or slaked lime), $Ca(OH)_2$, and dolomitic hydrate, $Ca(OH)_2.MgO$ in the furnace injection process has also been studied. Pressure is required to produce the completely hydrated dolomite, $Ca(OH)_2.Mg(OH)_2$.

Sodium-based sorbents sometimes considered include nahcolite and trona. Nahcolite is a naturally occurring material consisting primarily (>80%) of sodium bicarbonate ($NaHCO_3$). It is expensive and not readily available. Trona consists of sodium carbonate and sodium bicarbonate, $Na_2CO_3.NaHCO_3.2H_2O$. The sodium-based materials, although efficient SO_2 removers, can create severe waste handling problems due to their high solubility and the resulting waste leaching problems.

Calcium-based sorbents are the preferred injection materials and this report focuses primarily on limestone.

4.0 CHEMISTRY

The following reactions occur in a coal-fired boiler during combustion and after injection of limestone:

i) Sulfur in the fuel is oxidized primarily (>95%) to SO_2. A small fraction is oxidized to SO_3 (2-3%) or remains in the reduced state (H_2S). The extent of the reactions depends upon residence times, temperatures and the concentration of oxygen available.

ii) When limestone ($CaCO_3$) is injected into the furnace, time and heat are required to drive off the water and carbon dioxide to generate the active species, lime (CaO). This step is referred to as calcination.

iii) Once CaO is formed reaction with SO_2, sulfation, occurs. SO_2 will react with $CaCO_3$, however, to a much lesser degree.

The calcination and sulfation reactions are discussed in detail in the following sections.

4.1 Calcination

The reactions involved in the calcination of high calcium and dolomitic limestones are shown in equations 1 and 2.

$$CaCO_3 + \text{heat} \rightleftharpoons CaO + CO_2 \qquad (1)$$

high calcium quicklime

$$CaCO_3.MgCO_3 + \text{heat} \rightleftharpoons CaO.MgO + 2CO_2 \qquad (2)$$

dolomitic quicklime

Successful calcination is dependent upon three factors:

i) the stone must be heated to the dissociation temperature of the carbonates;

ii) this minimum temperature, or practically a higher temperature, must be maintained for a certain duration;

iii) the CO_2 evolved must be removed to prevent recarbonation.

The dissociation temperature of $CaCO_3$ is 898°C at 1 atm P in a 100% CO_2 atmosphere/5/. The decomposition temperature of dolomitic limestones is not as explicit. The magnesium carbonate component of dolomite decomposes at temperatures much higher than that of natural magnesite, $MgCO_3$, which dissociates at temperatures in the range 402-480°C, 1 atm P 100% CO_2. Since the proportion of $MgCO_3$ to $CaCO_3$ differs in the many species of dolomitic and magnesian limestones, the dissociation temperature also varies and is difficult to calculate. An average value for complete dissociation at 1 atm pressure in a 100% CO_2 atmosphere is

725°C/5/. The $CaCO_3$ component of dolomites does not, however, decompose until approximately 898°C (100% CO_2, 1 atm P) resulting in dual stage decomposition.

These calcination temperatures are not rigid and vary with the counteracting CO_2 pressure and concentration, see Figure 1 /5/. If the temperature and CO_2 pressure are in equilibirum, regardless of their values, dissociation is static. A minute change in one of these variables, ie, a decrease in CO_2 pressure or concentrations, or an increase in temperature, will cause dissociation to proceed immediately with evolution of CO_2 gas and simultaneous formation of oxides.

The theoretical minimum heat requirement to make a ton of lime from 100% pure $CaCO_3$ is approximately 2.77 million BTU/ton (3.22 x 10^9 Joules/metric ton). This is the heat requirement to retain the dissociation temperature until all of the CO_2 has been expelled. About 1.6 million BTU (1.69 x 10^9 Joules) is necessary to heat the stone to the dissociation temperature. The values are less for magnesian stone and dolomite. As the impurities increase in the stone, the thermal requirement is reduced correspondingly since there is less carbonate to decompose/5/.

As limestone is heated to its dissociation temperature, the free moisture in the stone is volatilized and the small amount of organic matter that exists in most limestones is ignited. These changes increase the porosity of the stone and add slightly to the heat requirement. At the point that calcination begins the stone may contain a myriad of micropores and crevices (fissures) interspersed throughout its crystal lattice. The $CaCO_3$ crystal lattice during preheating also undergoes thermal expansion prior to calcination, eg, increases of 5-10% in the linear dimensions of the matrices have been observed/5/. This expansion also helps to increase the stone's porosity.

Calcination proceeds gradually from the outside surface of the particle inward. The depth of penetration moves uniformly inward on all sides like a "growing" veneer or shell. The ideal stone for calcination is therefore small and of uniform size and shape. Some surface dissociation of the carbonate molecules can occur at temperatures below the dissociation point and lower partial pressures of CO_2, but in order for dissociation to penetrate into the interior of the stone, high temperatures are necessary. The larger the diameter of the stone, the higher the temperature required for dissociation of the core due to the increasing internal pressure as the CO_2 gas forces its escape. For stones of the same purity, the difference between dissociation temperature of the surface and the core may be 3-700°F (0-371°C) depending primarily on the stone's diameter/5/. In practice therefore, the temperature must generally be well in excess of the theoretical dissociation temperatures. The optimum calcination temperature, in terms of the amount of particle surface area produced, generally occurs at approximately 1000°C for both high calcium and dolomitic limestones/5/.

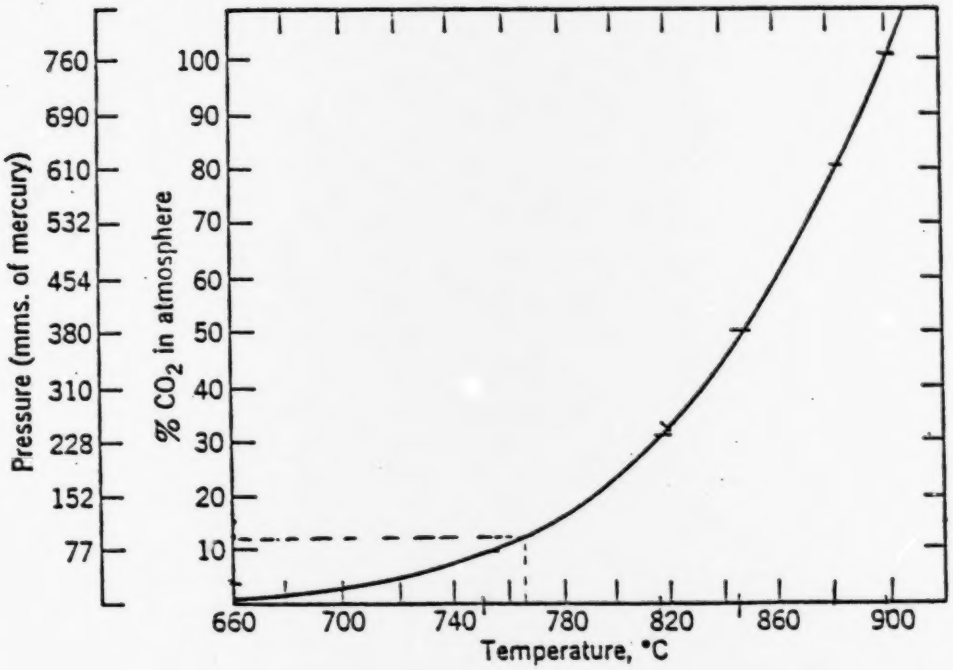


FIGURE 1

Influence of CO_2 Concentration and Pressure on Dissociation Temperature $CaCO_3$.

CaO after proper calcination is a porous, soft particle with low shrinkage, low density and high reactivity. Calcination at temperatures below 1100°C generally takes place without significant change of particle dimensions. More than half of the total particle volume is free pore space, giving the calcine a spongy texture/6/.

During prolonged calcination or calcination at elevated temperatures (T >1000°C) and/or pressures, the already calcined surfaces can become deadburned or sintered. Deadburning tends to shrink the stone, occluding or narrowing pores and fissures through which the CO_2 must escape, thus generating more pressure. Deadburned stone has a high density, low porosity and low chemical reactivity.

Prolonged calcination causes the CaO molecular crystal that formed through dissociation to simultaneously unite into progressively larger crystallites. As the temperature increases from 900 to 1000 to 1100°C a larger coherent mass of crystallites is formed. With increasing temperature the crystallites become steadily more strongly bonded together. The size of the average CaO crystal is reported to increase about a thousandfold (from 0.1 μm to 1000 μm) between initial calcination at the minimum dissociation temperature and the sintering temperature of ~3000°F (1649°C) when the lime is completely deadburned/5/. The grain growth caused by the sintering reduces the specific area, S_g, because

$$S_g = \frac{3}{r_g \rho_{CaO}} \qquad (3)$$

where r_g is the grain radius of nascent CaO formed immediately after $CaCO_3$ decomposition, and ρ_{CaO} is the absolute density of CaO/5/. Studies by Borgwardt et al suggest that CO_2 catalyses the CaO sintering process/7/.

The difference in decomposition temperature between $MgCO_3$ (725°C at 1 atm 100% CO_2) and $CaCO_3$ (898°C at 1 atm 100% CO_2) and the resulting prolonged exposure of MgO to high temperatures during the calcination of dolomites often results in the MgO fraction being deadburned in varying degrees before CaO is formed/5/.

The rate of heating has been found to have the greatest influence on the quality of the lime generated, more than the maximum temperature or residence time. Each limestone has an optimum calcination temperature and rate of heating that are best determined experimentally.

When limestone is injected into the boiler it is exposed immediately to temperatures considerably above its decomposition temperature. Surface areas of calcines prepared under boiler injection conditions, ie, small particles calcined in periods of less than 3 s in dispersed systems, have been reported to be an order of magnitude greater than those of calcines prepared at the same temperature by gradual heating/6/. Isihara reported surface

areas averaging 22 m^2/g for instantaneous calcination of limestone particles ranging in size from 3.4-49 μm. Coutant found surface areas as high as 53 m^2/g CaO when 50 μm particles were calcined in 0.15 s at 1230°C, but dropping to about 21 m^2/g after 1.3 s/7/. At high furnace temperatures sintering and deadburning occur rapidly causing considerable sorbent deactivation.

The physical and chemical properties of a calcine are also markedly influenced by the crystallite size of the parent limestone. The slowest stones to calcine (for a given size range) are dense, coarse crystalline limestones followed by finely crystalline materials. The coarse crystalline stones with their dense microstructure release CO_2 slowly since the gas has difficulty penetrating the dense crystal lattice. The pressure of CO_2 within the crystal must be very much greater than the external pressure. Large crystalline stones also do not conduct heat as readily as the more porous fine grained types. In the case of highly crystalline limestones, expansion of the crystal matrix during heating may completely disintegrate the stone to dust.

Dolomites also calcine easily and achieve higher surface area particles than those obtained with calcination of pure $CaCO_3$. Calcination of a mixture of $CaCO_3$ and $MgCO_3$ does not, however, yield particles similar in surface area to calcined natural dolomitic particles. The higher surface areas achieved with dolomites are due to the presence of $MgCO_3$ in the crystal lattice/8/. Recall that the $MgCO_3$ fraction decomposes at lower temperatures than $CaCO_3$ thereby causing particle breakup.

Complete thermal decomposition of 100% pure calcite results in a 44% weight loss. In the case of dolomite, the weight loss is greater since $MgCO_3$ will release 52.2% of its weight as CO_2 gas. Complete calcination is virtually impossible to attain. If lime is cooled prior to complete calcination of the core, there can still be a faint diffusion of CO_2 from the red hot core, which can be reabsorbed on the surface of the cooling lime resulting in recarbonation.

During calcination the pores of the particle can become clogged by the slagging effect of impurities in the stone, mainly SiO_2, Al_2O_3, that are fixed with lime forming occlusions. Clogging can cause shifts in dissociation conditions, recarbonation of the surface and/or incomplete dissociation of the core. This can yield dense, highly reactive lime with a low surface area but one which is underburned or uncalcined in the centre.

4.2 Sulfation

Calcined $CaCO_3$, ie, CaO, reacts rapidly with SO_2 and SO_3 to give $CaSO_4$ and $CaSO_3$, respectively, equations 4,5,6 and 7.

$$4CaO + 4SO_2 \rightarrow 3\ CaSO_4 + CaS \qquad (4)$$

$$CaS + 2O_2 \rightarrow CaSO_4 \qquad (5)$$

$$CaO + SO_2 \rightarrow CaSO_3 \quad (6)$$

$$CaO + SO_3 \rightarrow CaSO_4 \quad (7)$$

Sulfation is believed to occur in two stages, (i) reaction of SO_2 and O_2 with the exposed surface of lime, followed by (ii) diffusion of the gaseous reactants through the resultant shell of $CaSO_4$ to the core of the unreacted lime.

Studies of the limestone sulfation reaction reported by Borgwardt et al/6/ suggest that the reaction of limestone with SO_2 is first order with respect to the concentration of SO_2 in the gas phase. Work by Coutant et al suggests that the reactivity of the stone has little dependence on the SO_2 concentrations except at low levels/10/.

Kinetic studies of the sulfation reaction show that SO_2 capture increases with the square of the sorbent surface area/11/. The largest contributor to the stone's surface area is pores with diameters in the range 0.05-20 um. Pores in the calcine smaller than 0.1 um do not admit SO_2 rapidly enough to have a significant effect on the sulfation reaction during short exposure times.

In 1984 Borgwardt et al/7/ reported the results of a detailed study of the mechanisms of sulfur capture by limestone. They found that in the absence of pore diffusion effects, the reactivity of CaO with SO_2, H_2S and COS increases with the square of the specific surface area. The ultimate rate of the reaction is determined by diffusion through the product layer surrounding the CaO grains within a calcine particle.

The nature of the diffusion mechanism, ie, molecular versus ionic, was also investigated by Borgwardt et al/7/. If the gases are molecularly transported through the product layer, the overall rate of reaction would be expected to increase in direct proportion to the partial pressure of the reacting gas and the effect of temperature would be slight. An Arrhenius type plot of rate data would yield an apparent activation energy of approximately 5 kcal/mole. The experimental results showed good agreement with the Arrhenius relationship over the full range of temperatures studied. The diffusivity of the product layer increased exponentially with temperature and an activation energy of 37 kcal/mole was calculated. This high activation energy implies that the diffusing species are not gaseous and that the reaction is chemically controlled. These results, together with the observation that the rate of sulfation is independent of the partial pressure of the gas, suggest that the diffusion process controlling the rate of transport of sulfur species through the product layer surrounding the CaO grains within a calcine particle involves the movement of ions, not gas.

Studies of the sulfation of sorbents such as pressure hydrated dolomites and hydrated high calcium limestones ($Ca(OH)_2$) have also been reported. Beittel et al/12/ found that sulfur removal efficiency decreases in the series, pressure hydrated dolomites >

calcium hydroxide > dolomite > calcium carbonate. However, when mass feed rate is plotted versus SO_2 removal, the pressure hydrated dolomite was equivalent to calcium hydroxide and dolomite was equivalent to calcium carbonate. The dolomites suffer a weight basis penalty due to the presence of inert magnesium. Analysis of sulfated dolomitic samples shows that sulfation of magnesium is negligible/12/. The improved performance of $Ca(OH)_2$ relative to $CaCO_3$ is generally ascribed to a more porous calcine being produced during calcination of $Ca(OH)_2$ relative to that derived from $CaCO_3$.

Temperature affects both the rate of the sulfation reaction and the decomposition of the sulfur-alkali product. $CaSO_4$ begins to decompose at 2192°F (1200°C), $CaSO_3$ at 1332°F (722°C) and $MgSO_4$ at temperatures around 1598°F (878°C)/3/. These temperatures however, signal only the start of decomposition, a particle's stability is a function of both its residence time and temperature.

4.3 Additives

Alkali metal salts have been found to enhance calcium sorbent utilization and sulfur capture. Rakes et al/13/ reported that sodium carbonate increased limestone sulfur capture by 6-12% when used at a level of 5 weight per cent of the sorbent. Borgwardt also reported that Na_2CO_3 enhanced SO_2 capture and the improvement increased with the amount added but not in direct proportion. The actual contribution of the Na_2CO_3 to SO_2 capture was relatively minor, at the 5% level it accounted for about 7.5% of the total sulfur capture while the CaO conversion doubled. Cr_2O_3 also significantly enhances SO_2 capture/7/.

Borgwardt et al/7/ investigated the mechanism of Cr_2O_3 and alkali metal salt enhancement of SO_2 capture by the sorbent. Compounds such as Li_2CO_3, Na_2CO_3, $KHCO_3$ etc were found to significantly increase the rate of diffusion and the rates were higher at low temperature, ie, 800°C vs 1125°C. Li_2CO_3 increased the reactivity of CaO to such an extent that 100% conversion was obtained. The chloride ion was found to inhibit sorbent SO_2 capture. The results suggest that some additives reduce the activation energy of the calcination or sulfation reaction.

Three mechanisms were proposed to explain the observations:

i) the additive causes a reduction in the rate of CaO sintering;

ii) the additive increases the rate of SO_2 oxidation; or

iii) the additive increases the rate of ionic diffusion.

Mechanism (i) was eliminated because Cr_2O_3 and alkali salts such as M_2CO_3, M = Na,K, Li and Na_2SO_4, etc accelerate sintering. The SO_2 oxidation mechanism was eliminated because, in the case of Cr_2O_3, it must be in contact with CaO in order for activation to

occur. In addition, compounds such as V_2O_5 and Fe_2O_3, both known catalysts of SO_2 oxidation, were found to be very poor CaO reactivity promotors when compared to noncatalysts such as Na_2SO_4.

The rate of ion diffusion, mechanism (iii) is determined by the concentration of defects in the atomic lattice, ie, product layer. Defects may be substitutionally or thermally induced. Substitutional defects can be caused by the presence of certain foreign metal oxides or salts on the particle surface. If metal salts are incorporated into the growing product layer, the induced defect could increase ionic mobility and reduce the activation energy of diffusion through the product layer. Substitutional defects generally enhance diffusion most strongly in the lower temperature regions where thermal defects are less dominant.

The results obtained by Borgwardt et al/7/ are most consistent with the additives acting to promote the reactivity of CaO by inducing defects in the growing product layer and thereby increasing ionic diffusivity.

Although a number of materials have been shown to promote sorbent SO_2 capture, the additives must be nontoxic both before entering the boiler and after, and they must be cheap. Cr_2O_3 is not an acceptable promotor because it is very toxic. Sodium-based additives, eg, Na_2CO_3, have a threshold addition limit of 5 weight per cent. Above this level fouling in the boiler can become a problem. There is, therefore, still scope for development of a safe, nontoxic and cheap additive.

5.0 SORBENT FURNACE INJECTION

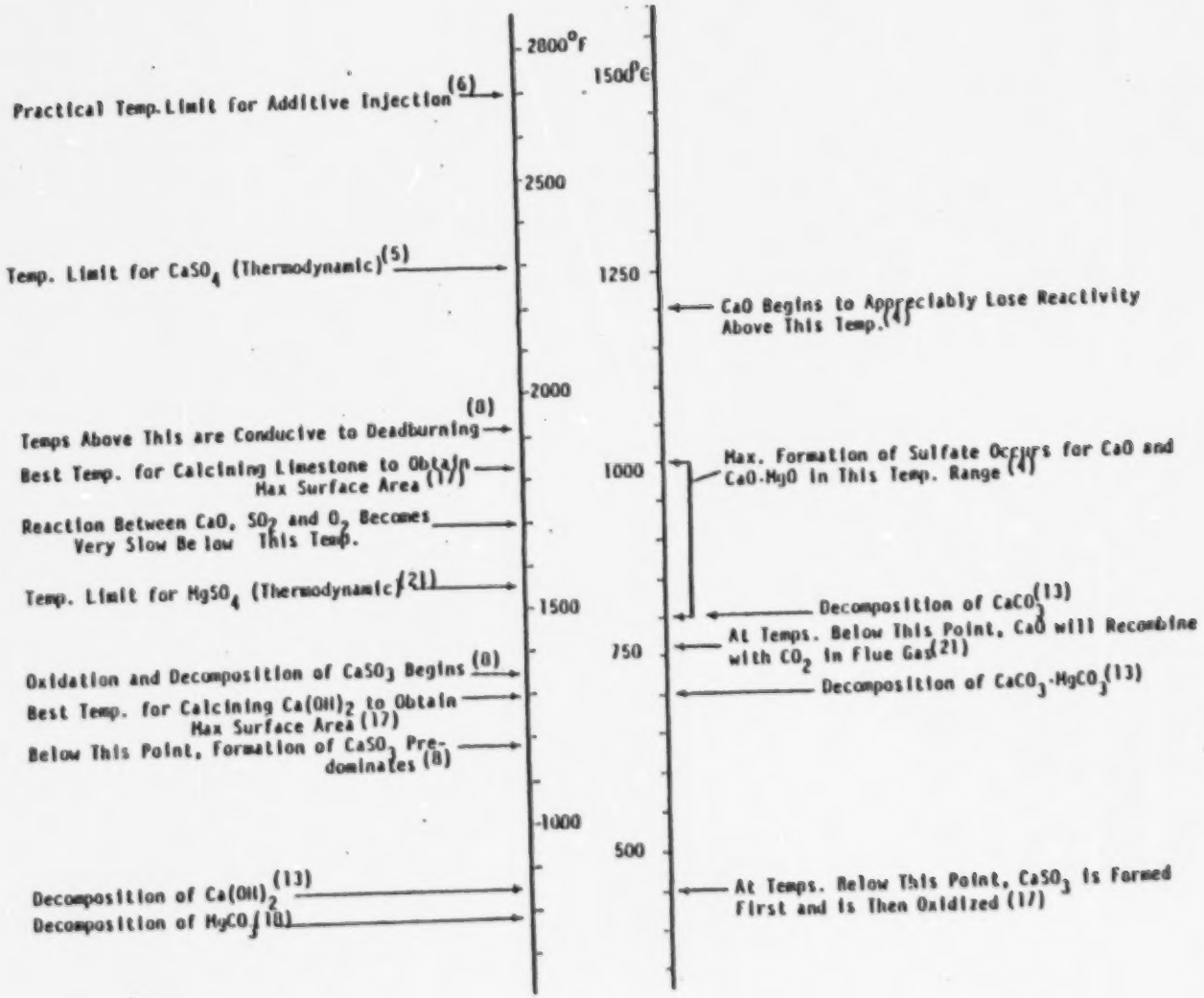
Sections 4.1 and 4.2 described factors which control limestone calcination and sulfation reactions in general. The temperature dependence of these reactions is summarized in Table 1/3/. This section examines the conditions in a coal-fired boiler which may affect the overall efficiency of sulfur capture by limestones.

5.1 Sorbent Sulfur Capture in a Coal-Fired Boiler

When limestone is injected into a coal-fired furnace, reaction of $CaCO_3$ and CaO with sulfur containing species other than SO_2 can also become important. A coal-fired boiler has two zones, an oxygen deficient reducing zone and an oxidizing zone. The reducing zone is the area in and around the flame. Its length is determined by the rate of pyrolysis of the coal particles injected into the combustor, the rate of heat transfer achieved and the level of mixing of air and combustibles/14/. In the low NO_x burner a less turbulent flame zone relative to that in conventional burners is produced by delaying the initial mixing of coal and air, and creating an O_2 deficient, ie, reducing, primary combustion zone which inhibits NO_x formation/15/. The dominant sulfur containing species in this zone are H_2S and COS. Sulfur capture may occur by reaction of H_2S with $CaCO_3$ or CaO to give CaS, eg, equation 8/16/,

TABLE I

Temperature Milestones/3/


2800°F
1500°C
Practical Temp. Limit for Additive Injection (6)
2500
Temp. Limit for $CaSO_4$ (Thermodynamic) (5)
1250
CaO Begins to Appreciably Lose Reactivity Above This Temp. (4)
2000
Temps Above This are Conducive to Deadburning (8)
Best Temp. for Calcining Limestone to Obtain Max Surface Area (17)
Max. Formation of Sulfate Occurs for CaO and CaO·MgO in This Temp. Range (4)
1000
Reaction Between CaO, SO_2 and O_2 Becomes Very Slow Below This Temp.
Temp. Limit for $MgSO_4$ (Thermodynamic) (21)
1500
Decomposition of $CaCO_3$ (13)
At Temps. Below This Point, CaO will Recombine with CO_2 in Flue Gas (21)
750
Oxidation and Decomposition of $CaSO_3$ Begins (8)
Best Temp. for Calcining $Ca(OH)_2$ to Obtain Max Surface Area (17)
Decomposition of $CaCO_3 \cdot MgCO_3$ (13)
Below This Point, Formation of $CaSO_3$ Predominates (8)
1000
500
Decomposition of $Ca(OH)_2$ (13)
At Temps. Below This Point, $CaSO_3$ is Formed First and is Then Oxidized (17)
Decomposition of $MgCO_3$ (13)

$$CaCO_3 + H_2S \longrightarrow CaS + CO_2 + H_2O \quad (8)$$

As oxygen is entrained into the flue gases, an oxidizing atmosphere is created and SO_2 becomes the predominant sulfur containing species.

The molar volumes of $CaCO_3$, CaO, $CaSO_4$ and CaS are listed below:

$CaCO_3$	34.16 cm^3/mole
CaO	16.49 cm^3/mole
CaS	28.86 cm^3/mole
$CaSO_4$	~45.99 cm^3/mole/14/.

As a CaO particle enters the H_2S containing gas in the combustion reducing zone, its surface is slowly converted to CaS. The porosity of the surface decreases due to the increased molar volume of CaS relative to CaO. As a result the accessibility of the interior pores to H_2S decreases and the apparent rate of sulfidation decreases. The decrease in pore accessibility is, however, even more significant in the case of sulfation since an expansion of 64.15% is observed when CaO is converted to $CaSO_4$/14/.

Since CaS is smaller than $CaCO_3$, the CaO formed by decomposition of $CaCO_3$ can be converted completely to CaS provided that the CaO particle has retained the original gross volume of the $CaCO_3$ particle. However, only 0.62 of CaO could be converted to $CaSO_4$, provided that the CaO particle does not shrink or expand. It would therefore be desirable to trap as much sulfur as possible on the sorbent in the reducing zone, since molar volume would not impose restrictions on the maximum conversion possible. It is assumed that during calcination, ie, during evolution of CO_2, no H_2S nor SO_2 molecules can approach the surface and no sulfurization of the solid occurs until the decomposition of the carbonate is complete. It would therefore be best, from a molar volume consideration, if calcination occurs completely in the reducing zone while the coal particle is still releasing H_2S, thereby facilitating rapid sulfidation of the CaO. A maximum amount of CaS can be formed if the heating rate of the coal and the limestone particles can be adjusted so that a maximum contact time is available for the H_2S and the CaO in the temperature range 800-1100°C/14/.

$CaSO_4$ is not very stable thermally and decomposes reasonably rapidly at temperatures above about 1323°K (1050°C)/14/. In coal-fired boilers $CaSO_4$ can undergo a number of side reactions. $CaSO_4$ reacts with clays and quartz in the temperature range 800-1400°C. Metal oxides such as Fe_2O_3, and potassium and sodium salts significantly increase the rate of decomposition of $CaSO_4$ and the rate of related reactions, eg, equation 9,

$$3\ CaSO_4 + CaS \xrightarrow{NaCl} 4\ CaO + 4\ SO_2 \quad (9)$$

In the presence of carbon, alumina reacts with $CaSO_4$ according to equation 10,

$$Al_2O_3 + CaSO_4 + C \longrightarrow CaO.Al_2O_3 + SO_2 + CO_2 \qquad (10)$$

Carbon and other reducing reagents initially accelerate the decomposition of $CaSO_4$ and also reduce it to CaS/14/. When a sufficiently thick CaS layer is formed on $CaSO_4$, the sulfate decomposition rate becomes diffusion limited and decomposition essentially stops. These results are substantiated by the finding that more sulfur is retained in coal ash and in calcium containing additives when unburned carbon is present in the ash. These decomposition reactions cannot be neglected when the ash or sulfated calcium additives spend appreciable time in zones where the temperature is >1000°C and/or where the coal or combustion additive contains significant amounts of potassium or sodium chloride/14/.

5.1 Factors Affecting Efficiency of Sorbent SO_2 Capture

The efficiency of sulfur capture by a sorbent injected into the coal-fired furnace is critically affected by a number of factors. These factors include:

i) the composition of the coal,

ii) furnace temperature at the point of sorbent injection,

iii) retention or residence time of particles in the furnace,

iv) mass transfer between SO_2 in the flue gas and sorbent particle,

v) sorbent feed rate,

vi) sorbent: coal sulfur stoichiometry,

vii) sorbent particle size.

The order of importance of these factors is unclear. Studies reported by TVA in 1973/17/ suggest that the two most important factors affecting SO_2 removal efficiency in the boiler are the rate of sorbent injection and the residence time of the sorbent in the optimum temperature range for the calcination and sulfation reactions, 1700°F (927°C) - 2200°F (1204°C). Boiler load as it affects particle residence time is also an important factor.

Coal composition, eg, moisture content and mineral composition, define the amount of heat released during combustion, ie, peak temperature in the burner flame zone. The mineral composition of the coal, ie, the alkalinity and sulfur content, determine the amount of sulfur captured by the coal ash and the concentration of SO_2 in the flue gas.

High sorbent feed rates cause a decrease in SO_2 removal efficiency, ie, decreasing per cent SO_2 removal per unit stoichiometry/17/.

High stoichiometries and small particle size are believed to improve absolute SO_2 removal. Approximately 75% of the variability of SO_2 removal can be attributed to the interaction of stoichiometry and particle size.

The optimum particle size for the limestone injection process is not clear. Some studies suggest particles of average size 50 μm, with no improvement in SO_2 removal observed with particles below 50-60 μm/3/. Other studies indicate that 10-15 μm particles are good. With limestone particles coarser than 100 mesh (~150 μm) the efficiency of limestone use is poor/18/. Particle size does, however, reach an optimum minimum by reason of grinding economics and the reduced particle pore surface transformations that occur when small particles are subjected to furnace gas conditions. If the grind is too fine, pore volume is destroyed.

Pulverization of limestone together with coal is difficult due to differences in the densities of the two materials, although better or equivalent SO_2 capture may be achieved relative to that obtained when the materials are ground separately/19/.

The turbulence of the furnace gas greatly influences and perhaps overrides the effects of a number of variables such as

- angle of sorbent injection,
- velocity of injection, and
- limestone particle size.

The location of sorbent injection is a critical element in the efficiency of the process. It dictates the temperatures to which the sorbent particles are subjected during calcination and influences the particle residence time in the furnace. The three basic criteria for injecting limestone in order to achieve the most beneficial results are:

i) maximize sorbent limestone residence time in the critical temperature region, ~900-1200°C;

ii) minimize time during which the limestone/sorbent particle is subject to deadburning;

iii) maximize mixing between limestone/sorbent and boiler gases.

A number of injection locations are possible: (i) with the coal; (ii) with the primary air; (iii) with the tertiary air or (iv) with a source of combustion air outside the burner area. The optimum injection location varies depending upon type of burner, the method of operation and the method of limestone injection. Furnace design is important as it affects the volumetric heat release rate and the heat flux within the furnace volume/19/.

Many studies describing the optimum injection location have been reported in the literature. The results initially appear contradictory. However, all experimental or furnace parameters must be considered before comparisons can be made.

Injection of sorbent through the coal nozzles, ie, with the coal, facilitates maximum mixing between the coal and limestone. This location requires minimum capital investment since existing coal nozzles are used. The primary disadvantage is that the sorbent suffers maximum exposure, ie, the longest possible residence time, to maximum furnace temperatures.

Takuda et al of Mitsubishi Industries Ltd/20/ reported that the optimum limestone injection location for their low NO_x burners was through the overfire air nozzle.

In the case of the CONOCO tests/21/, limestone was injected through the secondary air passage outside of the coal nozzle. 50% SO_2 reduction was demonstrated at a Ca/S molar ratio of 2.50-2.75. Equivalent calcium utilization was about 18-20%.

Sorbent injection outside of the burner zone is generally unsuccessful since temperatures in this region are too low to achieve limestone calcination/19/.

5.2 Effects on the Combustion System and Waste Materials.

Limestone furnace injection can cause a number of changes in the combustion system and in the properties and handling of the fly ash. Limestone in the furnace

- can alter the boiler temperature profile which may impact boiler efficiency;
- increases the solids loading which may result in convection pass plugging and accompanying draft losses, increased tube erosion, greater sootblowing requirements and increased particulate emissions;
- alters the chemical composition of the solids which may result in increased furnace slagging, tube corrosion and decreased electrostatic precipitator performance;
- increases the resistivity of the fly ash which also impedes ESP performance;
- gives the fly ash more cementitious properties than ordinary fly ash;
- can potentially affect solid waste disposal requirements due to the increase in solid wastes with a different chemical composition/22/.

The behaviour of limestone in a boiler is, however, dependent upon the total effect of variables such as

- the design and operation of a particular boiler, eg, combustion rates, flame temperature, fuel-air ratios, etc;
- particle fineness;
- particle residence time; and
- the extent of decomposition of the coal minerals and sorbent constituents and their reformation into other compounds.

In West Germany, injection of limestone into a brown coal burning boiler caused a change in the boiler heat transfer pattern due to the more opaque atmosphere in the combustion chamber. A slight increase in the flue gas exit temperature of 5-10°C, downstream of the air preheater was measured/22/. An increase in deposit formation was observed and the air preheater tended to foul more readily. No decrease in efficiency of the electrostatic precipitator was monitored immediately, but the voltage increased by up to 10% above the normal operational value without sorbent injection after several days of high sorbent addition rates. A build up of a deposit layer on the plattens was observed and could not be completely removed even by enhanced rapping cycles.

The increase in solids loading as a result of furnace limestone injection generally requires increased operation of the sootblowers and the ash conveying system. The system must be completely dry to facilitate sootblowing and to avoid plugging.

The extent of the decrease in efficiency suffered by the electrostatic precipitators is a function of

- limestone particle size
- flue gas temperature
- coal sulfur content, and
- the rate of limestone injection.

Flue gas conditioning with water in combination with the use of low ash coal has been found to alleviate some of the problems and reduce boiler limestone injection base emissions/21/. The reduction in precipitator efficiency and the capital costs associated with upgrading precipitators to maintain a preinjection level of efficiency can be a serious drawback to the limestone injection process.

Limestone in the fly ash requires changes in the methods of handling and disposal of the waste. High concentrations of free CaO in the ash tend to hydrolyze immediately in the presence of water. Steam is generated due to the exothermic CaO hydration reaction and the ash handling and transportation systems are endangered by the condensation of the water vapour and subsequent

corrosion. There is a time dependent hardening of the ash during transport. These problems can be somewhat alleviated by temperature controlled hydration of the total ash prior to handling for disposal or further utilization.

Addition of limestone to the furnace may either increase or decrease the average ash fusion temperature. In the case of limestone injection into a furnace burning Western coals, eg, Saskatchewan lignite, which have a relatively high sodium content, limestone increases the ash fusion temperature/23/. This causes a decrease in slagging and fouling problems in both the furnace and superheater. For other fuels, eg, Eastern bituminous, high iron, low alkaline earth content, addition of limestone may substantially decrease the ash fusion temperature and cause increased rates of slagging and fouling even in boiler regions not normally subjected to deposits/18/. The results of a detailed laboratory scale study of the effects of limestone on the ash fusion temperatures of a number of coals were reported in 1983/3/.

Limestone in the sluice water affects the pH, the dissolved solids concentration and hardness/17/. Dissolution of some limestone-based trace heavy metals in the effluent could cause environmental problems. If the limestone types used in dry scrubbing are limited to those with low levels of such metals, the sorbent costs could increase/17/.

6.0 CONCLUSIONS

A literature review of the dry limestone furnace injection method of control of SO_x emissions from coal-fired boilers has been presented. Despite the fact that few full-scale tests have been reported and SO_x removal efficiencies at the pilot scale are low, the relatively low cost of the process and the ease with which it can be applied to existing power plants has encouraged researchers to look at ways of optimizing the process. The number of variables which affect the efficiency of SO_x removal via limestone furnace injection make optimization a very site specific task.

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